

not exceeding 4.0 produced no defective charging, exhibited high charging and discharging efficiencies, and excelled in charging and discharging characteristics, whereas the batteries, A3, A4, and A5, having Li-Si ratios exceeding 4.0 produced defective charging due to an internal short-circuit resulting from the occurrence of dendrite and suffered low charging and discharging efficiencies.

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(Table 1)

Battery	Li/Si	Discharging capacity (mAh)	Ratio of occurrence of defective charging
A1	3.6	22.3	0
A2	4.0	25.5	0
A3	4.26	26.0	Very slight
A4	4.5	25.3	Small
A5	5.2	23.2	Medium

(Example 3)

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This example concerns a case of using manganese dioxide MnO_2 as a positive electrode active material. A battery was manufactured by following the procedure of Example 2 while using a positive electrode, a negative electrode, and a liquid electrolyte manufactured as described below in the place of the positive electrode 15, the negative electrode 13, and the liquid electrolyte of Example 2 and giving the electrode an outside diameter of 6.8 mm and a thickness of 2.1 mm.

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The positive electrode was manufactured as follows. The $\gamma + \beta$ - MnO_2 which was obtained by heat-treating electrolyte manganese dioxide MnO_2 in the open air at 400°C for six hours was used as an active material. A positive electrode agent was formed by mixing this active material with graphite as a conducting agent, a cross-linked acrylic acid resin as a binding agent, and a fluorine resin at a gravimetric ratio of 80 : 15: 5. Then, this positive electrode agent was press molded under 2 tons/cm² to produce a pellet, 4.05 mm in diameter and 0.69 - 0.87 mm in thickness. This pellet was dried under a decreased pressure at 150°C for 10 hours to obtain a positive electrode.

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The same agent as used in Example 2 was press molded under 2 tons/cm² to produce pellets, 4.05 mm in diameter and 0.24 - 0.40 mm in thickness. The pellets were used each as the negative electrode. A disc, 14 mm in diameter, punched out of a lithium film of a prescribed thickness was attached by contact superposition to the pellet to produce a lithium-negative electrode pellet laminate electrode.

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The electrolyte to be used was what was obtained by solving LiPF6 at a ratio of 1 mol/liter in a mixed solvent consisting of ethylene carbonate and ethyl methyl carbonate at a volumetric ratio of 1 : 1.

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In this example as in Example 2, two batteries B1 and B1 having molar ratios Li/Si respectively of 4.0 and 6.0 were manufactured, wherein Li stands for the amount of lithium superposed on the negative electrode and Si for the amount of silicon in the negative electrode active material. Further, the negative electrode agent, the amount of superposed lithium, and the positive electrode agent were adjusted so as to set the molar ratio Li/Mn at about 1 (0.91 - 0.99), wherein Li stands for the maximum amount of lithium released from the negative electrode and contained in the positive electrode in consequence of discharging.

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The batteries thus manufactured were subjected to charging and discharging cycles performed under the conditions, 0.1 mA in constant current, 3.3 V in terminal charging voltage, and 2.0 V in terminal discharging voltage. The charging and discharging characteristics found herein are shown in Fig. 9 and Fig. 10.

It is clearly noted from Fig. 9 and Fig. 10 that the battery B1 of this invention having a Li/Si ratio not exceeding 4.0 produced no internal short-circuit, incurred only a small decrease in the capacity for discharging, and excelled in the charging and discharging characteristics.

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(Example 4)

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This example concerns a case of using as a positive electrode agent a transition metal oxide preparatorily containing lithium. A battery was manufactured by following the procedure of Example 2 while using a positive electrode, a negative electrode, and a liquid electrolyte manufactured as described below in the place of the negative electrode 13, the positive electrode 15, and the liquid electrolyte of Example 2.

The negative electrode was manufactured as follows. The same agent as used in Example 2 was press molded under 2 tons/cm² to produce negative electrode pellets, 15 mm in diameter and 0.11 - 0.20 mm in thickness. The neg-

ative electrode pellet was attached to a negative electrode case with the aid of a negative electrode collector formed of a conducting adhesive agent using carbon as a conducting filler and they were dried under a decreased pressure at 200°C for 10 hours. Then, a disc, 12 - 14 mm in diameter, punched out of a lithium film of a prescribed thickness was attached by contact superposition to the negative pellet to produce a lithium-negative electrode laminate electrode.

The positive electrode was manufactured as follows. In a mortar, lithium hydroxide LiOH • H₂O, cobalt carbonate CoCO₃, and boron oxide B₂O₃ weighed out in amounts calculated to set a molar ratio of Li : Co : B at 1 : 0.9 : 0.1 were thoroughly mixed. The resultant mixture was fired in the open air at 850°C for 12 hours, cooled, pulverized to a particle diameter of not more than 44 µm, and subjected to dressing. By repeating the cycle of firing, pulverizing, and dressing twice, a positive electrode active material LiCo_{0.9}B_{0.1}O₂ according to this invention was synthesized.

A positive electrode agent was obtained by mixing the produced positive electrode active material with graphite as a conducting agent, a fluorine resin as a binding agent, and a cross-linked acrylic acid resin at a gravimetric ratio of 80 : 15: 5. Then, this positive electrode agent was press molded under 2 tons/cm² to produce pellets, 16.2 mm in diameter and 0.51 - 0.70 mm in thickness. These pellets were each dried under a decreased pressure at 100°C for 10 hours to produce a positive electrode.

The electrolyte to be used was what was obtained by solving lithium phosphate tetrafluoride LiPF₆ at a ratio of 1 mol/liter in a mixed solvent consisting of ethylene carbonate and diethyl carbonate at a volumetric ratio of 1 : 1.

In this example, 11 batteries were manufactured which had the amount of lithium superposed on the negative electrode and the amount of the positive electrode agent so adjusted that the molar ratio x_a of lithium superposed on the negative electrode to Si in the negative electrode active material, the molar ratio x_c of the amount of lithium releasable from the positive electrode (0.5 mol of lithium per mol of the positive electrode active material) to Si in the negative electrode active material, and the sum x_a + x_c might equal the values of Table 2.

The batteries thus manufactured were each left aging at room temperature for one week and then subjected to the following charging and discharging test. In consequence of this aging, the lithium-negative pellet laminate electrode as the negative electrode, on contact with the nonaqueous liquid electrolyte, formed one kind of local battery and the superposed lithium foil self-discharged, succumbed to occlusion into the SiO of the negative electrode, and produced a lithium-containing silicon oxide Li_xSiO.

The batteries thus manufactured were subjected to charging and discharging cycles performed under the conditions, 1 mA in constant current, 4.2 V in terminal charging voltage or 50 hours in duration of charging, and 2.0 V in terminal discharging voltage. The condition of occurrence of defective charging (abnormal variation of charging voltage) presumably due to an internal short-circuit formed in consequence of deposition of lithium dendrite is shown in Table 2. The charging and discharging characteristics of the batteries, C6 and C7, are shown in Figs. 11 and 12. The charging and discharging cycles were started from discharging.

It is clearly noted from Table 2, Figs. 11 and 12 that the batteries, C1, C3, C5, C6, C8, and C9, of this invention having total amounts of lithium x's not exceeding 4.0 in Li_xSiO_y of the negative electrode during the charging produced no defective charging, exhibited high charging and discharging efficiencies, and excelled in charging and discharging characteristics, whereas the batteries, C2, C4., C7, C10, and C11, having x's exceeding 4.0 produced defective charging due to an internal short-circuit resulting from the occurrence of dendrite and suffered low charging and discharging efficiencies.

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(Table 2)

	Battery	Superposed Li/Si X_a	Positive electrode Li/Si X_c	Total amount of Li, $x (X_a + X_c)$	Ratio of occurrence of defective charging
5	C1	0	4.0	4.0	0
	C2	0	5.9	5.9	Large
10	C3	0.5	3.4	3.90	0
	C4	0.5	3.75	4.25	Small
15	C5	1.5	2.1	3.6	0
	C6	1.5	2.5	4.0	0
20	C7	1.5	3.0	4.5	Small-Medium
	C8	2.0	1.5	3.5	0
25	C9	2.0	2.0	4.0	0
	C10	2.0	2.5	4.5	Medium
30	C11	2.0	3.9	5.9	Large

(Example 5)

25 This example concerns a case of using the following positive electrode active material and the liquid electrolyte in the place of the positive electrode active material and the liquid electrolyte of Example 4. Batteries were manufactured by following the procedure of Example 4 while using the positive electrode active material and the liquid electrolyte mentioned above instead.

30 The positive electrode active material in this example was manufactured as follows. In a mortar, lithium hydroxide $\text{LiOH} \cdot \text{H}_2\text{O}$, cobalt carbonate CoCO_3 , and silicon dioxide SiO_2 weighed out in amounts calculated to set a molar ratio of $\text{Li} : \text{Co} : \text{Si}$ at $1 : 0.9 : 0.1$ were thoroughly mixed. The resultant mixture was fired in the open air at 850°C for 12 hours, cooled, pulverized to a particle diameter of not more than $44 \mu\text{m}$, and subjected to dressing. By repeating the cycle of firing, pulverizing, and dressing twice, a composite oxide having an approximate composition of $\text{LiCo}_{0.9}\text{Si}_{0.1}\text{O}_{2.05}$ was obtained as a positive electrode active material of this example.

35 The electrolyte to be used was what was obtained by solving LiPF_6 at a ratio of 1 mol/liter in a mixed solvent consisting of ethylene carbonate and ethyl methyl carbonate at a volumetric ratio of 1 : 1.

When the batteries obtained as described above were subjected to a charging and discharging cycle test in the same manner as in Example 4 under the conditions, 1 mA in constant current, 4.2 V in terminal charging voltage, and 40 2.0 V in terminal discharging voltage, they showed decreases of 15 - 25% in the capacity for charging and discharging and a decrease in the ratio of occurrence of defective charging. When the total amounts of lithium x in the Li_xSiO_y of the negative electrode exceeded 4.0, however, defective charging occurred owing to the formation of dendrite.

(Example 6)

45 This example concerns a case of using a lithium-containing manganese oxide as a positive electrode active material. A battery was manufactured by following the procedure of Example 3 while using the positive electrode and the liquid electrolyte manufactured as described herein below in the place of the positive electrode and the liquid electrolyte of Example 3.

50 The positive electrode was manufactured as follows. Electrolyte manganese dioxide MnO_2 , lithium hydroxide, and lithium nitrate weighed out in amounts calculated to set the molar ratio of $\text{Mn} : \text{Li}$ at $1 : 0.3$ were mixed. The product obtained by heat-treating the resultant mixture in the open air at 400°C for six hours was used as an active material (hereinafter referred to briefly as "d1"). A positive electrode active material was obtained by mixing this active material with graphite as a conducting agent, a cross-linked acrylic acid resin as a binding agent, and a fluorine resin at a gravitational ratio of 87 : 10 : 3. Then, this positive electrode agent was press molded under 2 tons/cm² to produce a pellet, 4.05 mm in diameter and 0.83 mm in thickness. The pellet was dried under a decreased pressure at 150°C for 10 hours to produce a positive electrode.

55 The electrolyte to be used was what was obtained by solving LiPF_6 at a ratio of 1 mol/liter in a mixed solvent con-

sisting of ethylene carbonate and ethyl methyl carbonate at a volumetric ratio of 1 : 1.

Further, the negative electrode agent, the amount of superposed lithium, and the positive electrode agent were adjusted so as to set the molar ratio Li/Si at 3.1, wherein Li stands for the amount of lithium superposed on the negative electrode and Si for the amount of Si in the negative electrode active material, and the molar ratio Li/Mn at 0.73, wherein 5 Li stands for the total of the maximum amount of lithium contained in the positive electrode in consequence of discharging and the amount of lithium preparatorily contained therein and Mn for the amount of manganese in the positive electrode.

A battery D1 was manufactured as described above. For comparison, a battery D2 was manufactured by following the procedure used for the manufacture of the battery D1 while using as a positive electrode active material (d2) the γ

10 β -MnO₂ obtained by heat-treating electrolyte manganese dioxide in the open air at 400°C for six hours.

The batteries thus manufactured were subjected to charging and discharging cycles under the conditions, 0.1 mA in constant current, 3.3 V in terminal charging voltage, and 2 V in terminal discharging voltage. The capacities for discharging found in the second cycle and the 100th cycle are shown in Table 3.

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(Table 3)

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Battery	Capacity for discharging (mAh)	
	Second cycle	100th cycle
D1	2.17	1.61
D2	1.27	0.55

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It is clearly noted from Table 3 that the battery D1 using the lithium-containing manganese oxide as a positive electrode active material exhibited a large capacity for charging and discharging, incurred only a small decrease in the capacity for charging and discharging due to the repetition of charging and discharging, and excelled in charging and discharging characteristics as compared with the battery D2 using MnO₂ not preparatorily containing lithium.

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Industrial Applicability

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As described in detail above, this invention contemplates using as a negative electrode active material for a non-aqueous electrolyte secondary battery a lithium-containing silicon oxide represented by a compositional formula Li_xSiO_y with the lithium content x and the oxygen content y regulated so as to satisfy respectively the expressions, 1.5 ≤ x ≤ 4 and 0 < y < 2 and, consequently, allows production of a secondary battery excelling in charging and discharging characteristics exhibited at a large current. The secondary battery obtained by this invention exhibits a high efficiency of charging and discharging, precludes the occurrence of such defects as an internal short-circuit due to the occurrence of dendrite, and offering an extremely stable and long cycle life.

40 **Claims**

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1. A nonaqueous electrolyte secondary battery composed at least of a negative electrode, a positive electrode, and a lithium ion-conducting nonaqueous electrolyte, characterized by using as a negative electrode active material a lithium-containing silicon oxide represented by a compositional formula Li_xSiO_y with the lithium content x and the oxygen content y regulated so as to satisfy respectively the expressions, 1.5 ≤ x ≤ 4 and 0 < y < 2.
2. A nonaqueous electrolyte secondary battery according to claim 1, wherein said negative electrode uses as an active material a lithium-containing silicon oxide Li_xSiO_y having a lithium content x in the range of 2 ≤ x ≤ 4 and said positive electrode uses as an active material a transition metal oxide not containing lithium prior to the assembly of said battery and destined to contain lithium in consequence of discharging after the manufacture of said battery or during the manufacture of said battery.
3. A nonaqueous electrolyte secondary battery according to claim 1, wherein said negative electrode uses as an active material a lithium-containing silicon oxide Li_xSiO_y having a lithium content x in the range of 1.5 ≤ x ≤ 3.9 and said positive electrode uses as an active material a transition metal oxide containing lithium.
4. A nonaqueous electrolyte secondary battery according to claim 1 or claim 3, wherein said positive electrode active material is a composite oxide represented by the compositional formula Li_aT_bL_cO_d, wherein T stands for at least

one transition metal element selected from the group consisting of Co, Ni, Mn, Fe, V, W, Nb, and Ti, L stands for at least one element selected from the group consisting of B, Si, P, Mg, Zn, and Cu, and a, b, c, and d respectively satisfy the expressions, $0 < a \leq 1.15$, $0.8 \leq b + c \leq 1.3$, $0 \leq c$, and $1.7 \leq d \leq 2.5$.

- 5 5. A nonaqueous electrolyte secondary battery according to claim 1 or claim 2, wherein said positive electrode active material is a manganese dioxide which has been heat-treated at a temperature in the range of 300 - 450°C.
- 10 6. A nonaqueous electrolyte secondary battery according to any of claims 1, 2, and 5, wherein said secondary battery uses manganese dioxide as a positive electrode active material and enables said manganese dioxide to occlude lithium and form a lithium-containing manganese oxide in consequence at least of discharging and enables said lithium-containing manganese oxide to release lithium in consequence of charging and the contents of lithium in the positive electrode and the negative electrode are so regulated that the lithium content x of said lithium-containing manganese oxide per mol of manganese falls in the range of $0 \leq x \leq 1$ in either of the states of charging and discharging.
- 15 7. A nonaqueous electrolyte secondary battery according to claim 1 or claim 3, wherein said positive electrode active material is a lithium-containing manganese oxide represented by the compositional formula Li_xMnO_y (wherein, x and y respectively satisfy the expressions, $0 \leq x \leq 4$ and $1 \leq y \leq 3$).
- 20 8. A nonaqueous electrolyte secondary battery according to claim 7, wherein the contents of lithium in the positive electrode and the negative electrode are so regulated that the lithium content x of said lithium-containing manganese oxide per mol of manganese falls in the range of $0.05 \leq x \leq 3$ in either of the states of charging and discharging.
- 25 9. A nonaqueous electrolyte secondary battery according to any of claims 1, 3, 7, and 8, wherein said positive electrode active material is a product obtained by heat-treating lithium and manganese in their simple substances or in the forms of oxides, hydroxides, or salts such as carbonates or nitrates or the like, mixtures thereof, or coprecipitates thereof at a temperature in the range of 300 - 1100°C.
- 30 10. A nonaqueous electrolyte secondary battery according to claim 9, wherein said positive electrode active material is a product obtained by heat-treating a mixture or coprecipitate of at least one member selected from the group consisting of oxide, hydroxide, and salts of lithium and manganese dioxide or a mixture thereof at a temperature in the range of 300 - 450°C.
- 35 11. A nonaqueous electrolyte secondary battery, characterized by using as a negative electrode active material a product obtained by causing a silicon oxide SiO_y (wherein y satisfies the expression, $0 < y < 2$) being electrochemically reacted with lithium or a lithium-containing substance to incorporate lithium ions into the silicon oxide SiO_y in amounts of a molar ratio of Li/Si in the range of 1.5 - 4.0, inside the battery after assembling the assembly of said battery or inside or outside said battery during the course of the production of said battery.

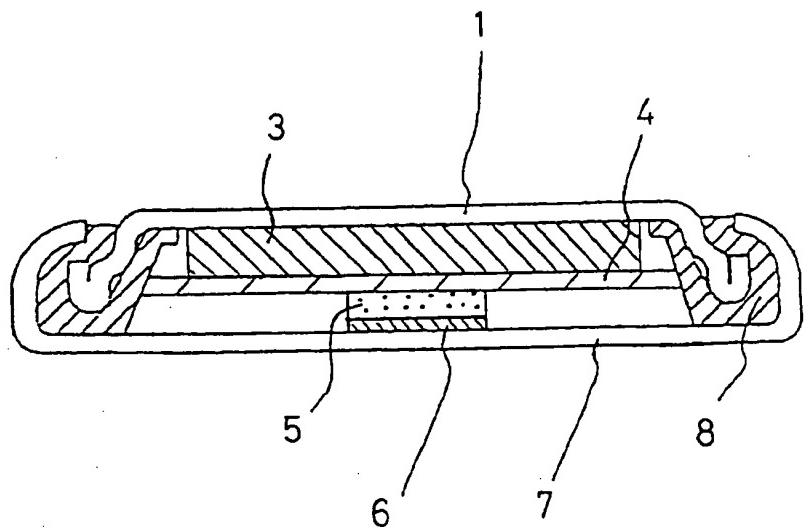
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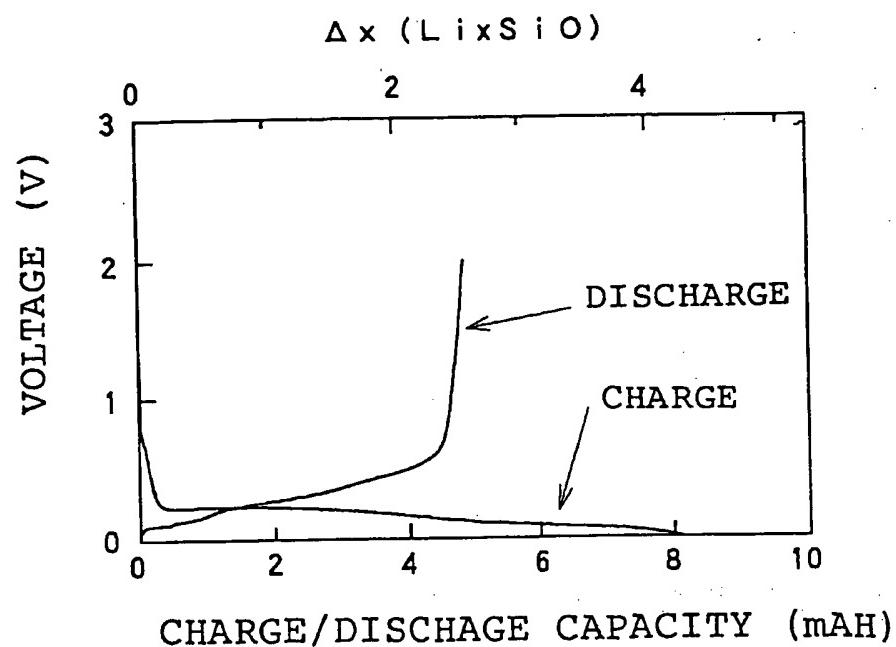
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FIG. 1



F I G. 2



F I G. 3

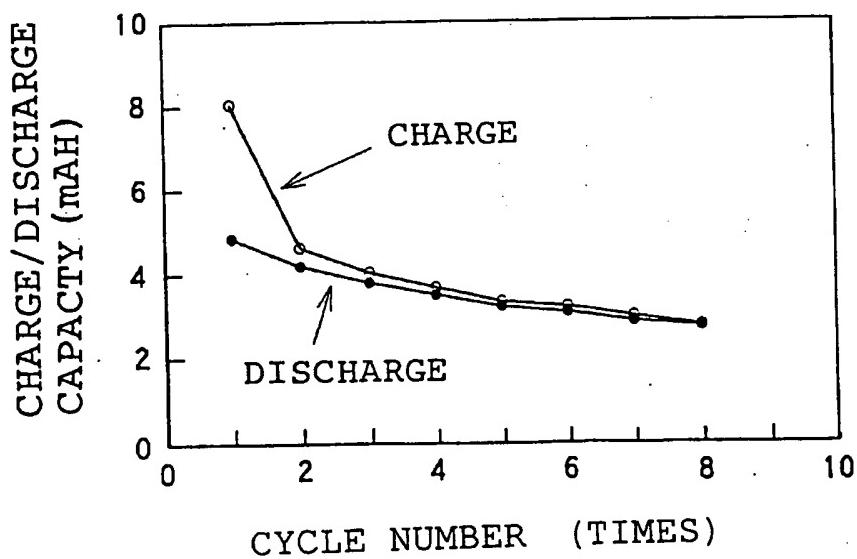


FIG. 4

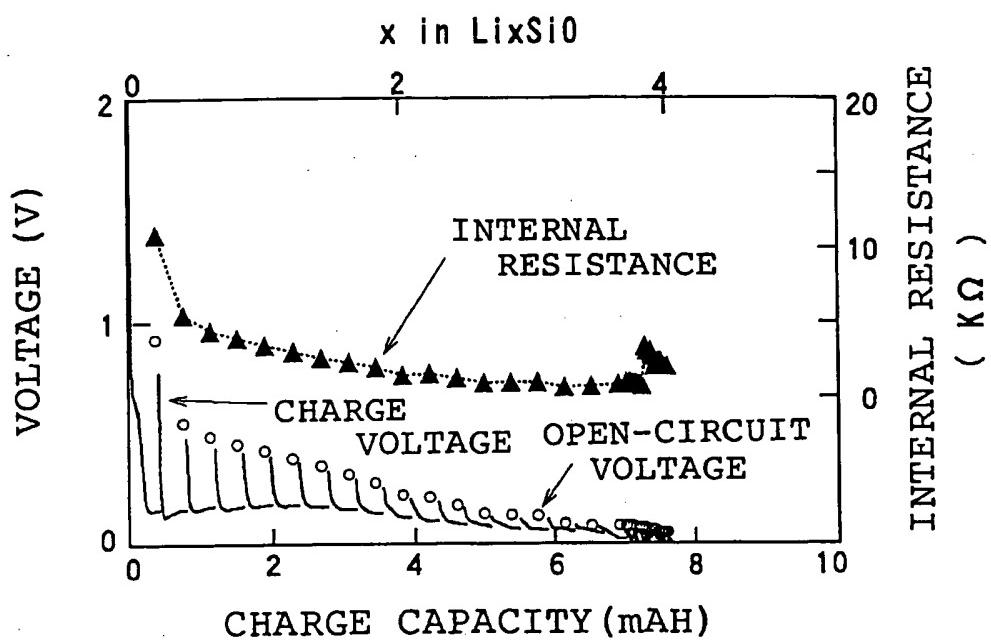
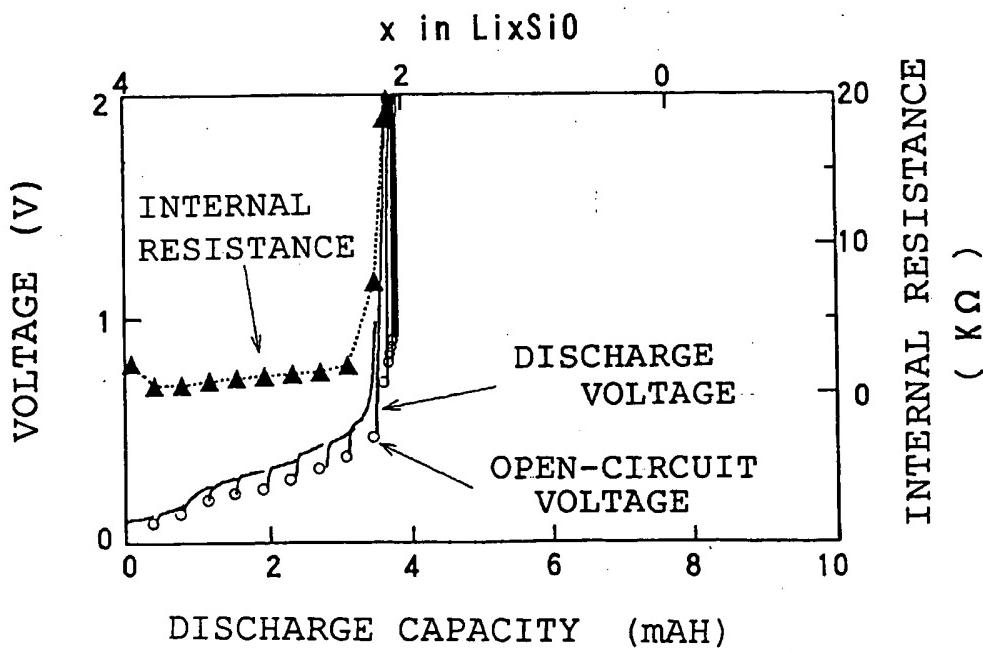


FIG. 5



F I G. 6

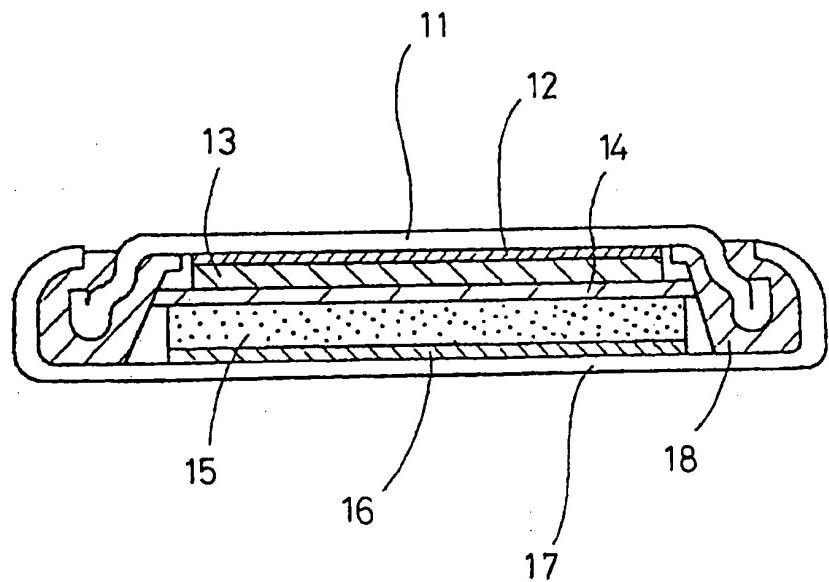


FIG. 7

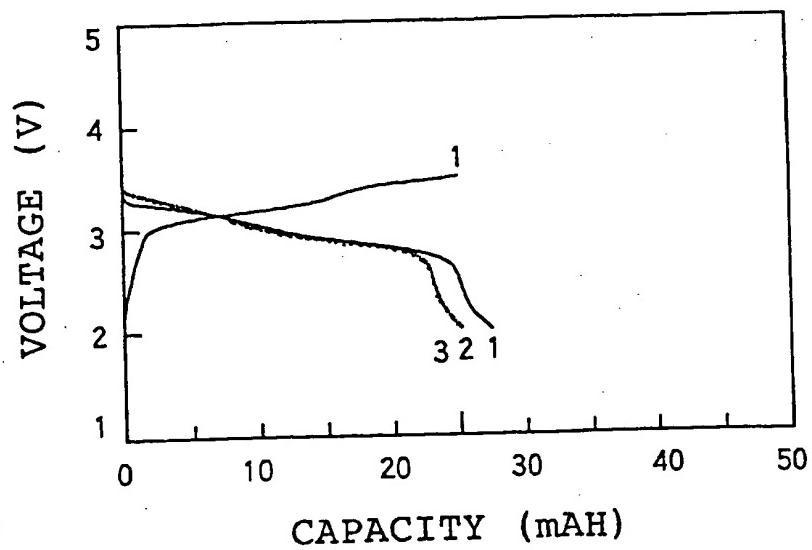


FIG. 8

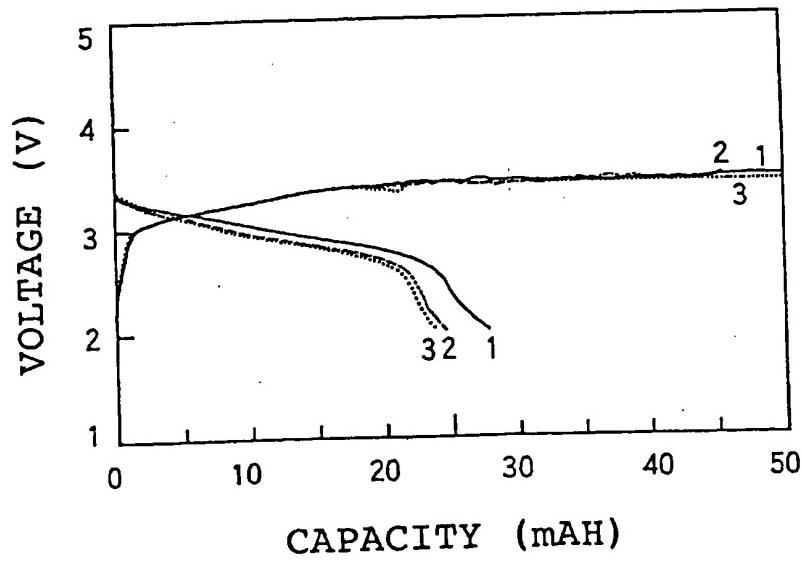


FIG. 9

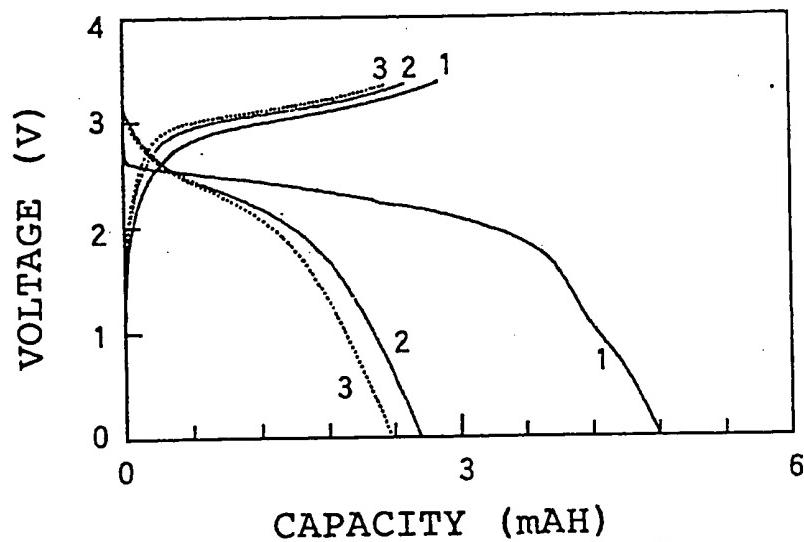
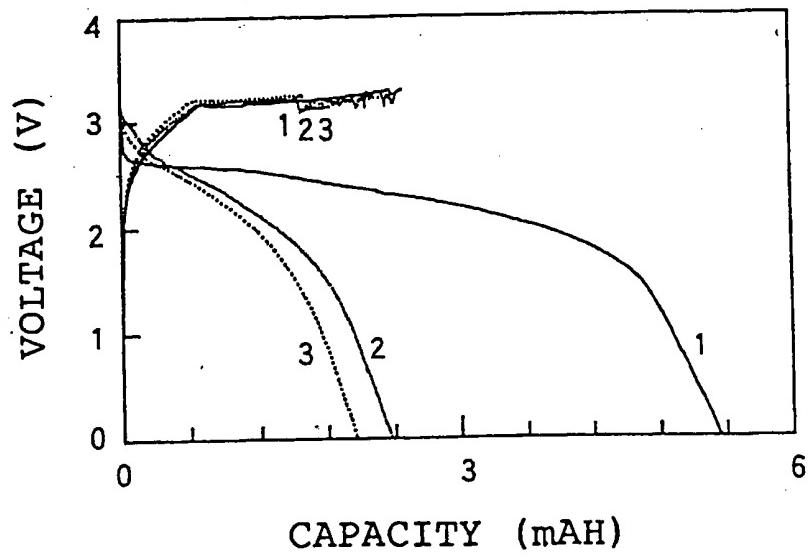
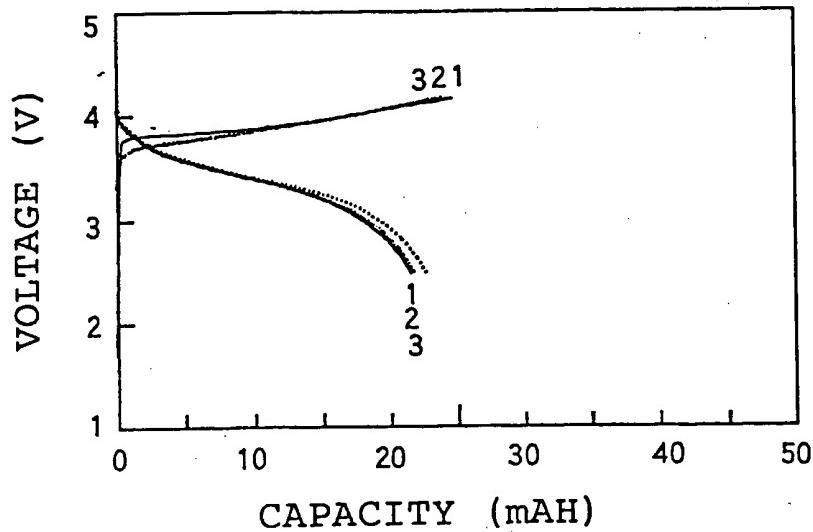


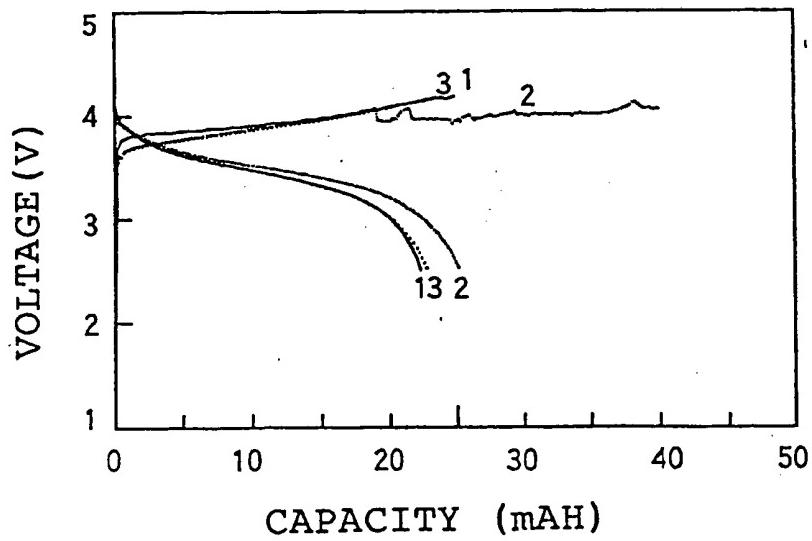
FIG. 10



F I G. 11



F I G. 12



INTERNATIONAL SEARCH REPORT		International application No. PCT/JP96/01744
A. CLASSIFICATION OF SUBJECT MATTER		
Int. C1 ⁶ H01M4/58 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int. C1 ⁶ H01M4/58		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926 - 1996 Kokai Jitsuyo Shinan Koho 1971 - 1995 Toroku Jitsuyo Shinan Koho 1994 - 1996		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 6-325765, A (Seiko Instruments Inc.), November 25, 1994 (25. 11. 94) (Family: none)	1 - 11
<input type="checkbox"/> Further documents are listed in the continuation of Box C.		<input type="checkbox"/> See patent family annex.
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Date of the actual completion of the international search September 6, 1996 (06. 09. 96)	Date of mailing of the international search report September 24, 1996 (24. 09. 96)	
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